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Naval Surface Warfare Center
Indian Head, MD 20640-5035

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SWELL RATIO TESTER REPORT FY 2003

Ralph Gamba

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This study examined the results of the SRT-1, and compared with the current sol-gel method of determining crosslink density at IHDIV/NSWC. We compared ease of use, time, material use, and the data from the two methods. This report provides the results of the comparison of the Swell Ratio Tester (SRT) with the current sol-gel method of determining swell ratio and crosslink density of polymers.

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FOREWORD

This report provides the results of the evaluation of the Swell Ratio Tester. This study compares the SRT-1 Swell Ratio Tester with the current method of determining crosslink density of polymers.

Ralph G. Gamba
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EXECUTIVE SUMMARY

Scope

This report provides the results of the comparison of the Swell Ratio Tester (SRT) with the current sol-gel method of determining swell ratio and crosslink density of polymers.

Objectives

This study examined the results of the SRT-1, and compared with the current sol-gel method of determining crosslink density at IHDIV/NSWC. We compared ease of use, time, material use, and the data from the two methods.

Results

The results show that the SRT-1 provided comparable results to the current method. In addition, the SRT-1 uses less solvent, less sample handling, and a smaller sample size. The SRT-1 measures swelling in a given direction, whereas sol-gel measures crosslink density by a gravimetric method. The main drawback is that the SRT-1 does not measure the dimension of the sample in the dried extracted state.

Conclusions

The SRT:

- Uses a smaller sample size than the sol-gel method (0.1 gram versus 0.7 gram).
- Uses less solvent than the sol-gel method (8 ml versus 300 to 400 ml).
- Takes less time than the sol-gel method (48 hours versus 144 hours).
- Requires less sample handling than the sol-gel method.
- Can only test one sample at a time. The sol-gel method can run 6 samples simultaneously, but the SRT can test six samples in approximately 1/3 the time it takes to perform the sol-gel testing on six samples.
- Results show good agreement and variance comparable with the sol-gel method.
- Can provide swell ratio at different temperatures.
- Assumes isotropic swelling. Polymers sometimes swell differently in different directions.

Recommendations

Continue the study by comparing the SRT-1 results to IHDIV/NSWC results on filled polymeric materials such as composite propellant such as PBXN-110, CKU5 liner, and Mk 104 booster propellant.

Investigate a modified SRT to determine the swell ratio in all three axes.

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OBJECTIVES

This study examined the use of the Swell Ratio Tester (SRT) as a tool to measure the crosslink density or swell ratio of polymers and compared the SRT to the current sol-gel method of determining swell ratio and crosslink density.

BACKGROUND

The swell ratio is used to measure the crosslink density of a polymer, which can assess its age and condition. A certain amount of crosslinking occurs in a polymer as it cures. Additional crosslinks can form as the polymer ages, resulting in degradation of mechanical properties. Depending upon the nature of the polymer and the environmental conditions, the crosslink density could conceivably increase or decrease with age, resulting in mechanical property changes that could affect the safety, reliability or performance of the item. The Cambridge Polymer Group developed a new method, the SRT-1, which uses lasers to measure the swelling of a polymer when placed into a solvent. According to the manufacturer, this method, in addition to being faster, more accurate, and more reliable, reduces exposure of the handler to volatile solvents. Because of these qualities, the SRT-1 could be a valuable tool in explosive surveillance.

A crosslinked polymer, when placed in a solvent, absorbs a portion of the solvent, causing it to swell. As the polymer chains elongate due to the swelling action, an elastic force is generated which opposes the deformation. The swelling ceases when the two forces reach equilibrium. The steady state swelling ratio is a direct function of the amount of crosslinking present in the polymer. Swelling experiments are a simple technique to characterize polymers. Simple measurements can be used for quality control, while more complex analysis can be used to calculate crosslink density, molecular weight between crosslinks and number of crosslink chains. See Appendix A for a detailed analysis of swelling measurements of crosslink density.

Current measuring techniques involve taking a sample of known weight and performing a soxhlet extraction for 72 hours, drying and immersing the sample into a solvent for 24 to 72 hours, and reweighing the sample. The swell ratio is the weight gained divided by the dried sample weight. The reduced swell ratio is the weight gained divided by the original sample weight. While this is a simple method, accuracy and reproducibility is difficult to achieve with volatile solvents (which tend to evaporate as the sample is being weighed), and unaccounted weight loss due to repetitive handling of the sample. Also, it can be difficult to determine when steady state is reached.

The Cambridge Polymer Group has developed the SRT-1, which uses a laser micrometer to measure the height of the sample. Assuming the sample swells isotropically, the swell ratio can be calculated from the change in height. This allows both transient and steady state ratios to be measured and does not require the sample to be removed from the solvent for measurement.

TEST PLAN

Cambridge Polymer Group received two lots of inert polybutadyene gumstock (51A1 and 341M) for testing using the SRT-1 Swell Ratio Tester. The Indian Head Division, Naval Surface Warfare Center (IHDIV/NSWC) prepared these samples by hand mixing. In addition, Cambridge Polymer Group tested aged gumstock from Lot 341M. The IHDIV analytical laboratory tested the same lots of gumstock using the sol-gel method to compare the two methods for ease of use and time of use. We also compared the data from the two methods and performed a statistical analysis to compare the variance on the resultant data.

The IHDIV representatives visited the Cambridge Polymer Group to witness the demonstration of the SRT-1.

RESULTS

A comparison of the two methods shows that the SRT-1 uses a slightly smaller sample, less solvent, takes less time and less sample handling than the sol-gel method. In addition, the SRT allows testing at different temperatures. One drawback to the SRT is that the SRT assumes isotropic swelling – uniform swelling in all directions. Non-isotropic swelling occurs when some polymers orient in a certain way due to manufacturing processes, such as the extrusion process. Otherwise, polymers generally are isotropic with respect to crosslink density. Our current methods of determining swell ratio and crosslink density also assume isotropic behavior. For nonisotropic swelling samples, each orientation must be tested separately.

For the current sol-gel method, the operator cut a disk of propellant approximately .1-inch by .5-inch diameter (~ .7 gram). Using chloroform, the operator performs a soxhlet extraction for 72 hours. The operator removes and places the sample in fresh solvent to equilibrate for approximately 72 more hours. The two extractions use a total of 300 to 400 milliliters of solvent. The operator then weighs the sample in a closed, dry container to minimize evaporation. The sample is then dried and weighed to determine the swell ratio. The swell ratio is calculated using the following equation:

$$q = \frac{W_d + (W_s - W_d)K}{W_d}$$

Where:

q = is the swell ratio;
W_d = is the initial or dry sample weight
W_s = is the swollen sample weight
K = is the ratio of solvent density to sample density

Using the final dried sample weight gives the swell ratio. If the initial sample weight is used in the calculation, one obtains the reduced swell ratio.

For the SRT-1, the operator cuts, measures and weighs a .2-inch x .2-inch x .2-inch cube (~.1 gram) of propellant. The sample is carefully placed into the SRT-1 chamber. The operator places the probe on top of the sample and calibrates the voltage for the initial height of the sample. Using a syringe, the operator injects 8 milliliters of solvent into the chamber and sets the temperature. The SRT-1 starts to collect the swell data. When the sample reaches equilibrium as recorded on the attached computer, the operator stops data acquisition. The software calculates the swell ratio and the crosslink density if the Flory interaction parameter is known. The software can calculate the crosslink density for gumstocks only. Filled or plasticized polymers require hand calculation. The crosslink density of filled or plasticized polymers requires the density, percentage and Flory interaction parameter of each ingredient. To have the software calculate the crosslink density of filled or plasticized polymers would require a major software modification at the manufacturer. Appendix A presents the equations used for the calculations.

Figures 1, 2, and 3 present the raw SRT-1 data from the three lots. The computer connected to the SRT generates the plots. The computer also calculates the swell ratio from the cubed ratio of the transient sample height normalized by the initial height. Lot 341M showed more variability in the results than Lot 51A1, thus Cambridge Polymer performed additional runs on Lot 341M to determine data spread. Lot 341M aged also showed some spread in the data. Appendix B provides the full SRT-1 test report.

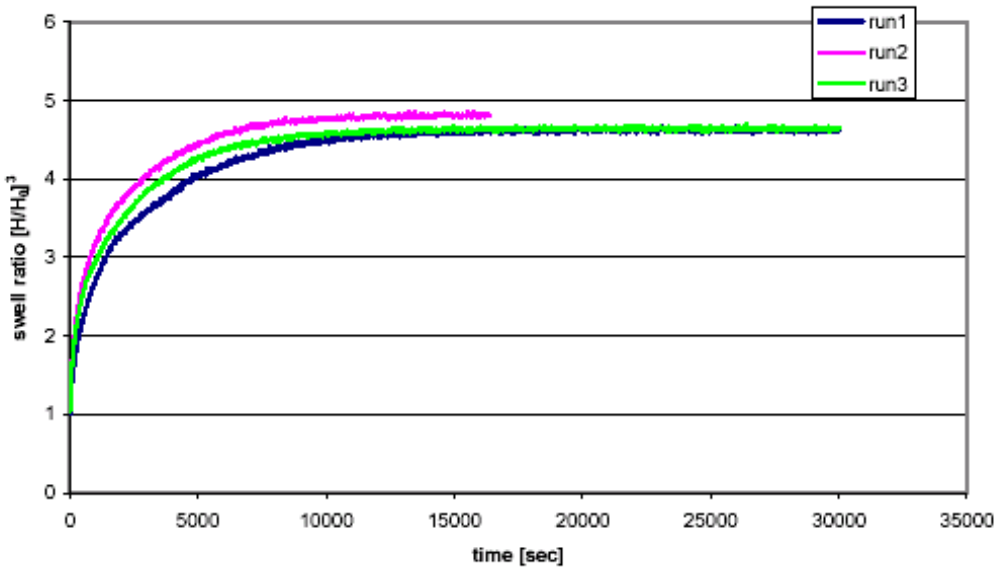

Figure 1. Raw Swelling Data for Lot 51A1

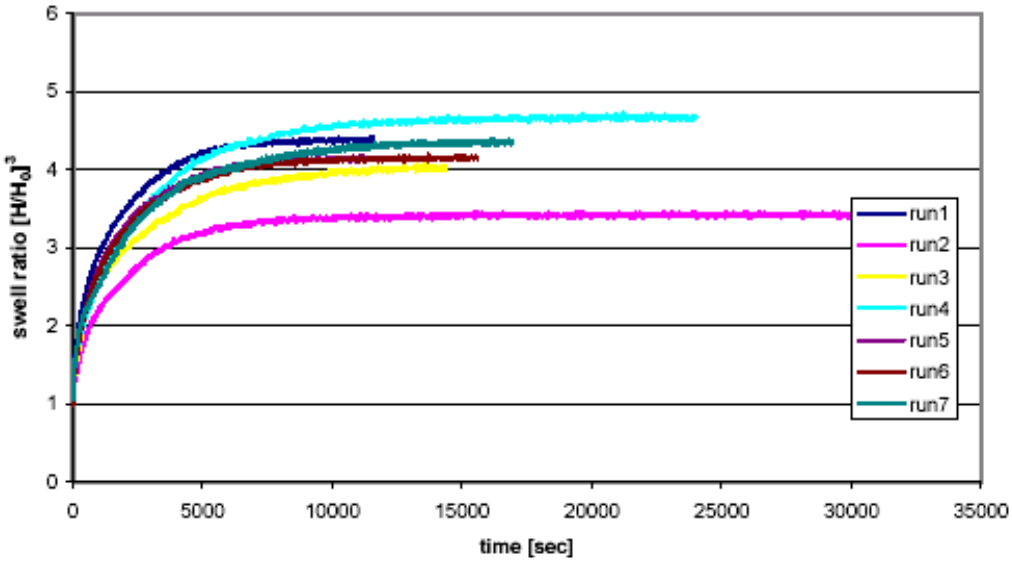

Figure 2. Raw Swelling Data for Lot 341M

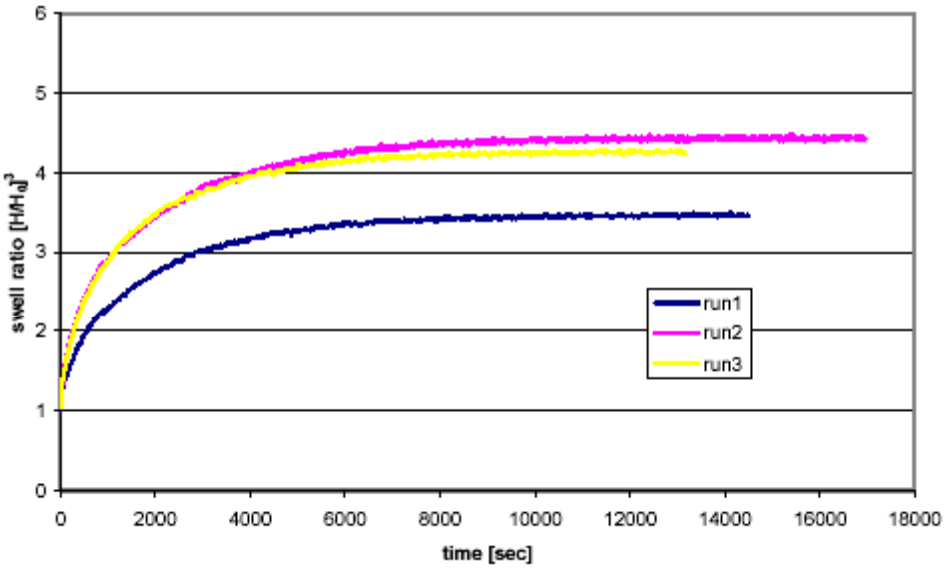

Figure 3. Raw Swelling Data for Lot 341M Aged

Table I shows the computed swell ratio for all the SRT runs. Individual runs that yielded data outside of the normal spread of data are indicated with an asterisk. Table II shows the average and standard deviations of the SRT-generated swell ratio, with and without the outliers removed.

Table I. Summarized SRT-Swell Ratio for Each Data Set

Sample	Run	Swell ratio (H/H_0)
51A1	1	4.62
	2	4.81
	3	4.64
	Average	4.69
	Stdev	0.10
341M	1	4.39
	2	3.39*
	3	4.02
	4	4.67*
	5	4.14
	6	4.15
	7	4.37
	Average	4.16
	Stdev	0.40
341M aged	1	3.47*
	2	4.26
	3	4.26
	Average	4.00
	Stdev	0.46

*statistical outliers.

Table II. Average and Standard Deviation of the SRT Swell Ratios

All data included	Average swell ratio	Standard deviation
51A1	4.69	0.10
341M	4.16	0.40
341M Aged	4.00	0.46
Outliers removed		
51A1	4.69	0.10
341M	4.21	0.16
341M Aged	4.26	0.00

Table III presents the swell ratio using the current method employed at IHDIV.

Table III. Results from the IHDIV Method

Lot 51A1	Sample wt. (g)	Swollen wt. (g)	Dried wt. (g)	% wt. loss	Reduced swelling ratio	Swelling ratio
1	0.2665	2.0319	0.2594	2.664	5.02	5.14
2	0.2505	1.905	0.2438	2.675	5.01	5.13
3	0.2731	2.0581	0.2661	2.563	4.96	5.08
4	0.2262	1.628	0.2218	1.945	4.76	4.84
5	0.2533	1.857	0.2477	2.211	4.84	4.94
6	0.2164	1.6055	0.2113	2.357	4.89	5.00
Average					4.91	5.02
Stdev.					0.10	0.12
Lot 341m, unaged	Initial sample wt. (g)	Swollen wt. (g)	Dried wt. (g)	% wt. loss	Reduced swelling ratio	Swelling ratio
1	0.2741	1.9915	0.2685	2.043	4.80	4.89
2	0.2853	2.0654	0.2792	2.138	4.78	4.88
3	0.2566	1.8535	0.2512	2.104	4.77	4.87
4	0.2434	1.6932	0.2389	1.849	4.61	4.69
5	0.2524	1.7639	0.2479	1.783	4.63	4.71
6	0.2193	1.5467	0.2151	1.915	4.67	4.75
Average					4.71	4.80
Stdev.					0.08	0.09

ANALYSIS

Comparing the two methods, the SRT-1 uses less solvent and less sample handling. With the SRT-1, the only handling is the cutting and placing the sample in the chamber and making sure the probe is on the sample where as the sol-gel sample is cut, extracted, tested and weighed while swollen. Solvent evaporation could affect the final results during the weighing process. In addition, with the SRT-1, the operator monitors the testing and determines when the sample reaches equilibrium, whereas with the sol-gel method, the operator must guess at the equilibrium time, usually 24 hours to 72 hours. The extraction process also lasts 72 hours. One disadvantage to the SRT-1 is that the operator can run only one sample at a time, whereas the sol-gel method can process 6 samples at a time. Six SRT-1 tests on this gumstock take approximately 48 hours versus 144 hours for the six sol-gel tests. However, this can vary depending upon the equilibration time for a given type of material and solvent.

The SRT-1 has a built-in heater, allowing the capability of testing samples at different temperatures. The sol-gel tests samples at room temperature.

The SRT-1 assumes the sample swells equally in all directions (isotropic). Closely monitoring the orientation and testing samples in the three orientations can overcome this deficiency. Because sol-gel is based on the weight of the sample, orientation effects are not discernable using sol-gel method.

The SRT-1 results from Lot 51A1 showed good reproducibility, while the data from Lot 341M showed a larger variation.

With the SRT-1, if all sample runs are included, there is no statistical variation in the swell ratio between the three lots. After removal of sample runs that are clearly outside of the mean data set, Lot 51A1 showed a significantly larger swell ratio than the 341M series. Lots 341M unaged and 341M aged showed no significant difference in swell ratio. The 341M series appears to have a higher degree of crosslinking than the Lot 51A1 sample.

Using the sol-gel method, the swell ratio for Lot 51A1 is greater than for Lot 341M, as seen with the SRT.

From Tables II and III above and using the F-test to compare the variances on the SRT-1 and IH swell ratio data, the sample variances for the SRT method and the sol-gel method are equivalent at the 95% confidence level. Thus, the two methods show good agreement and comparable variance.

These results are based on testing gumstock—basic polymer. Filled polymers such as liner material and composite propellants may act differently than gumstock.

CONCLUSIONS

- SRT uses a smaller sample size than the sol-gel method (0.1 gram versus 0.7 gram).
- SRT uses less solvent than the sol-gel method (8 ml versus 300 to 400 ml).
- SRT takes less time than the sol-gel method (48 hours versus 144 hours).
- SRT needs less sample handling than the sol-gel method.
- SRT can only test one sample at a time. The sol-gel method can run 6 samples simultaneously, but the SRT can test six samples in approximately 1/3 the time it takes to perform the sol-gel testing on six samples.
- SRT results show good agreement and variance comparable with the IHDIV method.
- SRT can provide swell ratio at different temperatures.
- SRT assumes isotropic swelling. Polymers sometimes swell differently in different directions.

RECOMMENDATIONS

Continue the study by comparing the SRT results to IHDIV results on filled polymeric materials such as composite propellant like PBXN-110, CKU5 liner, and Mk 104 booster propellant.

Investigate a modified SRT to determine the swell ratio in all three axes.

Appendix A

SWELLING MEASUREMENTS OF CROSSLINKED POLYMERS

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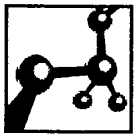

Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

Swelling Measurements of Crosslinked Polymers

Introduction

A crosslinked polymer, when placed in a good solvent, rather than dissolving completely, will absorb a portion of the solvent and subsequently swell. The swollen gel can be characterized as a solution, although it is an elastic one rather than a viscous solution. The extent of swelling represents a competition between two forces. The free energy of mixing will cause the solvent to penetrate and try to dilute the polymer solution. This entropic increase may be enhanced by increasing the temperature. As the polymer chains in the crosslinked polymer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The volumetric swelling reaches steady state when the two forces balance each other.

Given that the steady state swelling ratio is a direct function of extent of crosslinking in the sample, swelling experiments are a simple and low-cost technique to characterize polymer networks. At the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of crosslinking. At a higher level of analysis, the crosslink density, molecular weight between crosslinks, and number of crosslinks/chain can be computed if one knows the Flory interaction parameter for the polymer-solvent system.

Theory

The free energy chain of mixing when an isotropic polymer sample is placed in a pure solvent can be written in terms of the ordinary free energy of mixing ΔF_m and the free energy associated with expansion of the polymer network ΔF_{el} as

$$\Delta F = \Delta F_m + \Delta F_{el} \tag{1}$$

The free energy of mixing is described in terms of the number of solvent molecules n_1, the volume fractions of solvent and polymer, υ_1 and υ_2, and the Flory interaction parameter χ_1 as

$$\Delta F_m = kT\left[n_1 \ln \upsilon_1 + \chi_1 n_1 \upsilon_2\right] \tag{2}$$

The elastic component of the free energy ΔF_{el} is associated with the change in the entropy as the network is deformed, and can therefore be written in terms of the linear deformation factor α_s as

$$\Delta F_{el} = \left[kT\nu_e / 2\right]\left[3\alpha_s{}^2 - 3 - \ln \alpha_s^3\right] \tag{3}$$

where ν_e is the effective number of chains in the network. The chemical potential of the solvent in the gel is defined as

$$\mu_1 - \mu_1^0 = N\left(\partial \Delta F_m / \partial n_1\right)_{T,P} + N\left(\partial \Delta F_{el} / \partial \alpha_s\right)_{T,P}\left(\partial \alpha_s / \partial n_1\right) \tag{4}$$

where N is Avagadro's number. It is noted that $\alpha_s^3 = V/V_0$ where V_0 is the volume of the unswollen network and V the volume of the swollen network. Accordingly, $V_0/V = \upsilon_2$. Incorporating the molar volume of the solvent φ_1 to compute the solvent contribution to the volume yields the expression:

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$$\alpha_s^3 = 1/\upsilon_2 = (V_0 + n_1\varphi_1/N)/V_0 \tag{5}$$

Therefore, one can evaluate equation 4 with equations 3, 2, and 5 to yield:

$$\mu_1 - \mu_1^0 = RT\left[\ln(1-\upsilon_2) + \upsilon_2 + \chi_1\upsilon_2^2 + \varphi_1(v_e/V_0)\left(\upsilon_2^{1/3} - \upsilon_2/2\right)\right] \tag{6}$$

At equilibrium, the chemical potential of the solvent in the polymer will equal the pure solvent, so that the left side of equation 6 will be equal to zero. Rearranging equation 6 yields

$$-\left[\ln(1-\upsilon_2) + \upsilon_2 + \chi_1\upsilon_2^2\right] = \varphi_1(v_e/V_0)\left(\upsilon_2^{1/3} - \upsilon_2/2\right) \tag{7}$$

Rewriting the number of chains/unit volume in terms of the specific volume of the polymer $\bar{v}$ and the molecular weight between crosslinks M_c such that $v_e/V_0 = 1/\bar{v}M_c$, and further rearrangement gives the final expression for the crosslink density v_x.

$$\frac{1}{\bar{v}M_c} = v_x = -\frac{\ln(1-\upsilon_2) + \upsilon_2 + \chi_1\upsilon_2^2}{\varphi_1\left(\upsilon_2^{1/3} - \upsilon_2/2\right)} \tag{8}$$

Experimentally, one measures the swell ratio $q = V/V_0 = 1/\upsilon_2$ and, knowing the Flory interaction parameter (see Appendix A), computes the crosslink density and molecular weight between crosslinks $M_c = 1/\bar{v}v_x$.

Experimental Technique

Researchers use two principal techniques for measuring the swell ratio of crosslinked polymer networks. The first technique, a gravimetric approach, is discussed in ASTM D2765-95 (Method C). In this method, a sample is carefully weighed (W_d), then immersed in a solvent at the required temperature for 24 hours. At the end of this period, the sample is again carefully weighed (W_g), and the swell ratio is computed from this data and the ratio of the densities of the solvent to the polymer, K, as

$$q = \frac{W_d + (W_g - W_d)K}{W_d} \tag{9}$$

While this technique is a simple, low-cost approach to measuring the swell ratio, it is difficult to obtain accurate measurements when volatile solvents are used, since the solvent evaporates as the sample is being weighed. Additionally, it is difficult to determine when steady state is achieved.

Consequently, more researchers are turning to techniques that use a probe to measure the change in height of a sample as it swells. Assuming that the sample swells isotropically, the swell ratio is computed from the change in the height $H(t)$ as $q = (H/H_0)^3$. This technique allows one to measure both the transient and the steady state swell ratio and does not require the removal of the specimen from the solvent to make a measurement.

Cambridge Polymer Group has developed the *SRT-1*™, which uses a laser micrometer to measure the change in height of the sample. The *SRT-1*™ has been successfully used to measure swell ratios in crosslinked polyethylene, vulcanized rubber, and hygroscopic biopolymers.

In Figure 1, the swell response of radiation crosslinked ultra high molecular weight polyethylene in xylene at 130°C is shown. Steady state is reached after 150 minutes.

CPGAN # 005

Swelling Measurements of Crosslinked Polymers

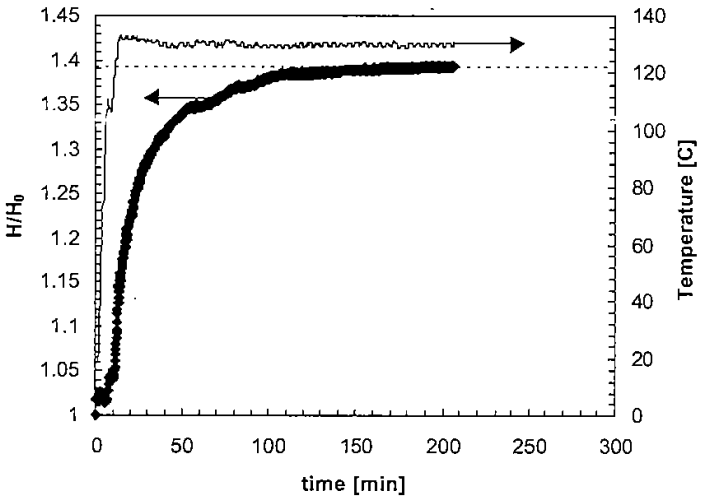

Figure 1: Transient change in height of radiation-crosslinked ultra high molecular weight polyethylene swelled in xylene at 130°C.

A series of samples with different molecular weight distributions were examined to determine the effects of polydispersity index (PDI = M_w / M_n) on crosslink density for identical levels of chemical crosslinking. The results of this study are shown in Figure 2.

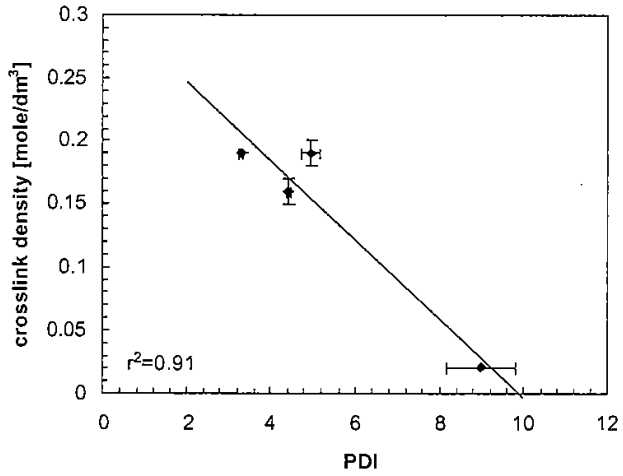

Figure 2: Dependence of crosslink density on polydispersity index of ultrahigh molecular weight polyethylene crosslinked with peroxide chemistry.

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Acknowledgements

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Appendix A: Determination of the Flory Interaction Parameter

Flory interaction parameters have been measured for a large number of polymer-solvent pairs. The determination of χ_1 is a time-consuming task, requiring careful measurements with a vapor-phase osmometer. In this technique, one places a dry, crosslinked sample against a sensitive thermister in the osmometer. Solvent is added, and the degree of swelling υ_2 is determined from volume uptake in the vapor compartment of the osmometer. At the same time, the temperature difference between the swelling sample and the reference solvent is measured, from which one calculates the chemical potential:

$$\mu_1 - \mu_1^0 = -\frac{LM_1}{RT_0^2}\Delta T \tag{10}$$

where L is the specific heat of evaporation of the solvent, M_1 is the molecular weight of the solvent, and T_0 is the reference temperature.

The only remaining unknown in equation 6 is the interaction parameter χ_1. Rearranging equation 6 yields

$$\frac{\frac{\Delta\mu_1}{RT} - \ln(1-\upsilon_2) - \upsilon_2}{\upsilon_2\varphi_1(v_e/V_0)(\upsilon_2^{1/3} - \upsilon_2/2)} = \chi_1\upsilon_2 \tag{11}$$

A series of measurements of $\Delta\mu_1$ vs. υ_2, and plotting the data with the left side of equation 11 vs. υ_2 should yield a straight line with a slope equation to χ_1, as shown in Figure 3.

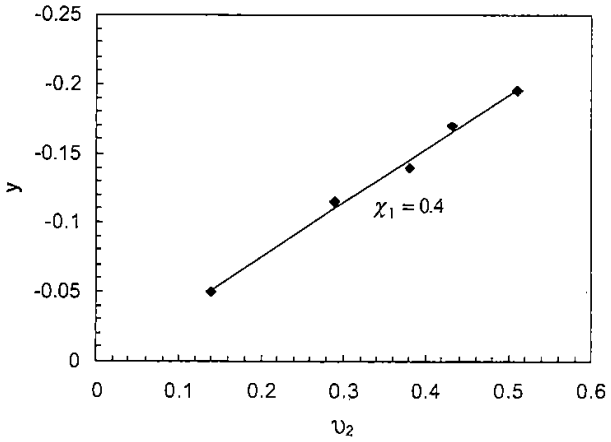

Figure 3: Plot of y (left side of equation 11) vs υ_2 for determination of the Flory interaction parameter.

Appendix B

SRT-1 TEST REPORT

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Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

Report 10260.1

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July 16, 2003

To: Christie Swanson, Bill Bryant
Naval Surface Weapons Center

Principal Investigator: Spiegelberg
Report Written: Spiegelberg
Reviewed by: Neal

Re: Swelling analysis on provided samples

1. Samples Submitted

Three sets of samples were received for swelling analysis. The samples were labeled as:

51A1 (2 disks)
341M (2 disks)
341M aged (1 disk)

The samples were approximately 1 cm in diameter, and 3 mm high.

2. Sample Preparation

The samples were sectioned into cubes approximately 3mm on a side, and oriented so that the original 3mm height was in the direction used to measure height change. The exact height for each specimen was measured with a digital micrometer with a resolution of 1 μm.

3. Instrument Conditions

The solvent was injected into the sample chamber after the data collection was initiated. The sample height was monitored until steady state conditions were achieved. All testing was performed in compliance with ASTM F2214-02. A minimum of 3 runs were conducted per sample.

Instrument:	SRT™ (Cambridge Polymer Group)
Software:	Version 2.2
Solvent :	Chloroform
Sample rate:	0.05 Hz
Temperature:	25°C

4. Data and Results

The raw data are summarized in Figures 1-3. The swell ratio is computed from the cubed ratio of the transient sample height H normalized by the initial height H_0. Sample 341M showed more variability in the results than 51A1; consequently, additional runs were conducted on this sample to determine the data spread. Similarly, 341M aged showed some spread in the data as well.

The computed swell ratios for all the runs are shown in Table 1. Individual runs that yielded results that were outside of the normal spread of data are indicated with an asterisk in this table. These data are removed in some of the later analyses.

The average and standard deviations of the swell ratios are shown in Table 2, with and without the outliers removed. These data are plotted in Figures 4 and 5.

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Single factor ANOVA analysis was conducted on both data sets (with and without outlier removal), and the results are summarized in Tables 3 and 4.

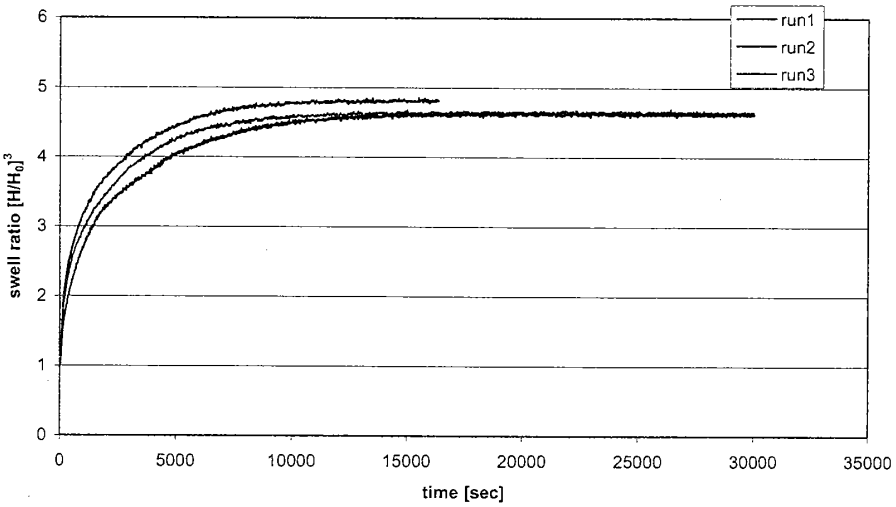

Figure 1: Raw swelling data for sample 51A1.

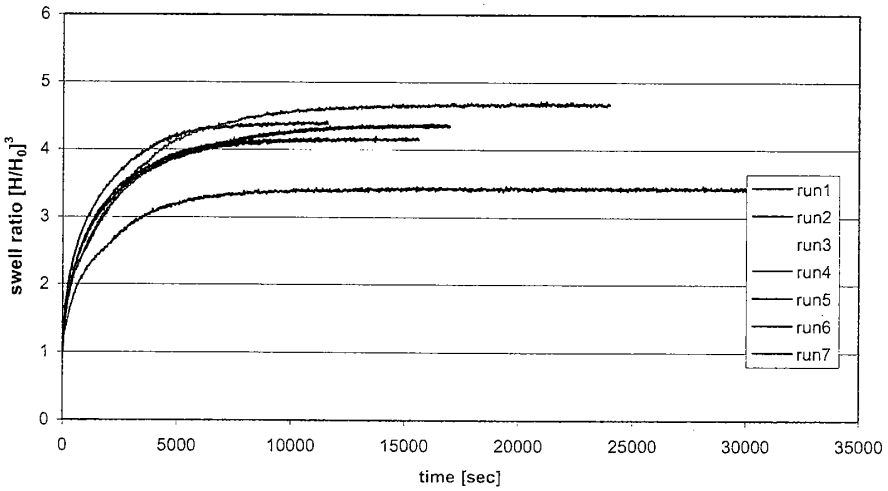

Figure 2: Raw swelling data for sample 341M.

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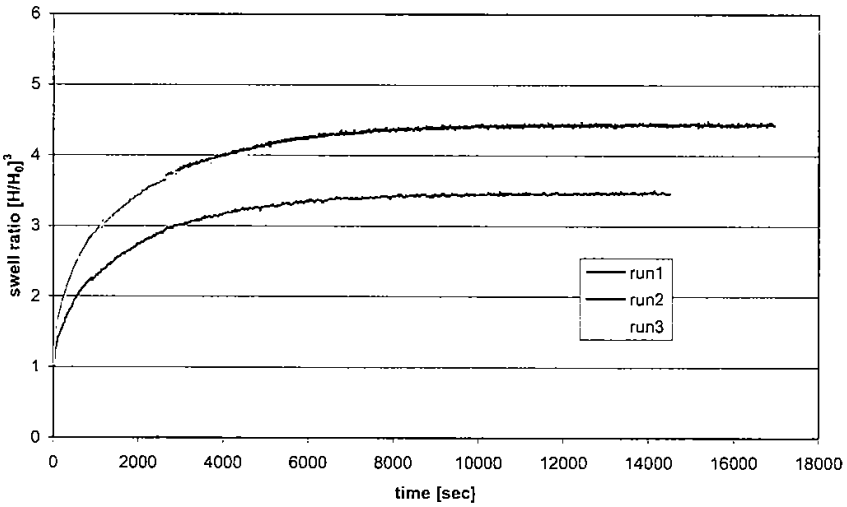

Figure 3: Raw swelling data for sample 341M aged.

Table 1: Summarized swell ratio for each data set

sample	run	swell ratio $[H/H_0]^3$
51A1	1	4.62
	2	4.81
	3	4.64
	average	**4.69**
	stdev	**0.10**
341M	1	4.39
	2	*3.39
	3	4.02
	4	*4.67
	5	4.14
	6	4.15
	7	4.37
	average	**4.16**
	stdev	**0.40**
341M aged	1	*3.47
	2	4.26
	3	4.26
	average	**4.00**
	stdev	**0.46**

*outliers that were removed for Figure 5 and Tables 2 and 4.

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Table 2: Average and standard deviations of the swell ratios. In the second set of data, the outliers shown in Table 1 were removed.

All data included	Average swell ratio	St. deviation
51A1	4.69	0.10
341M	4.16	0.40
341M aged	4.00	0.46
Outliers removed		
51A1	4.69	0.10
341M	4.21	0.16
341M aged	4.26	0.00

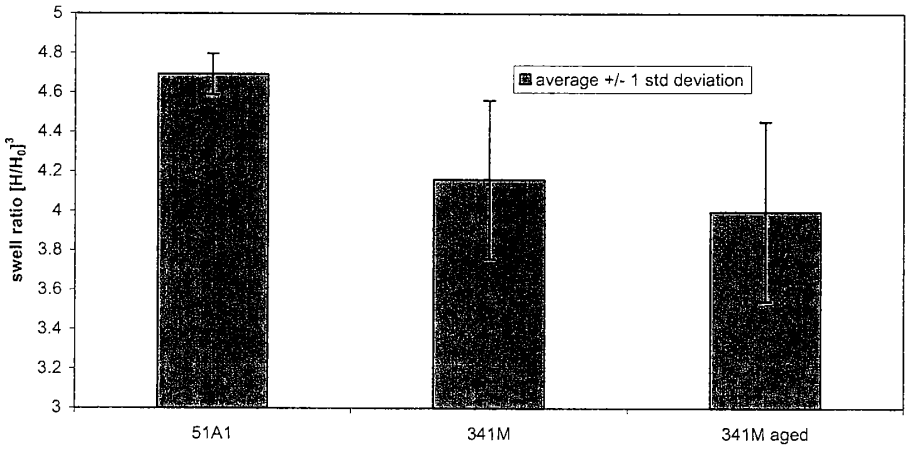

Figure 4: Summarized swell ratios for the three samples, including all data runs.

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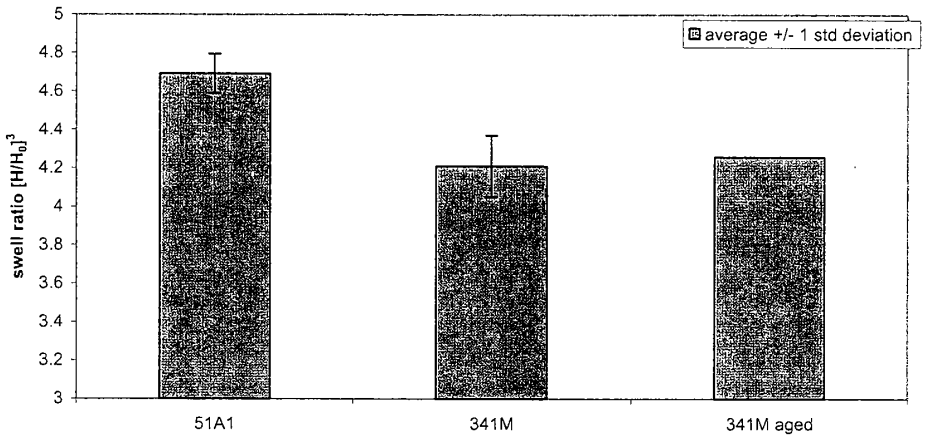

Figure 5: Summarized swell ratios for the three samples with outliers shown in Table 1 removed.

Table 3: Single Factor ANOVA analysis on all data sets.

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
51A1	3	14.07687	4.692289	0.010654		
341M	7	29.15132	4.164475	0.153143		
341M aged	3	11.99157	3.997188	0.20863		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.829731	2	0.414865	3.05626	**0.092084**	4.102816
Within Groups	1.357428	10	0.135743			
Total	2.187159	12				

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Table 4: Single Factor ANOVA analysis with outliers removed.

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
51A1	3	14.07687	4.692289	0.010654		
341M	5	21.05973	4.211945	0.025285		
341M aged	2	8.521799	4.260899	2E-07		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.46015	2	0.230075	13.15258	**0.004257**	4.737416
Within Groups	0.122449	7	0.017493			
Total	0.582599	9				

5. Discussion

Sample 51A1 showed good reproducibility in the three runs examined, while the 341M series showed a larger variation in results. The latter two sets of material are also characterized by a darker brown color. The variation in swelling results from the 341M sample could come from a intra-sample variation in crosslink density.

If all the conducted sample sets are included, there is no statistical variation in swell ratio between the 3 samples ($p > 0.05$). However, after removal of sample runs that are clearly outside of the mean data set, the ANOVA analysis indicates that 51A1 has a statistically significant larger swell ratio than the 341M series ($p = 0.004$), and that there is no apparent difference between 341M and 341M aged. The 341M series would appear to have a higher degree of crosslinking than the 51A1 sample.

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